

LUMINESCENCE SPECTRA OF BENZYL ACETATE IN THE SOLID STATE AT LOW TEMPERATURES

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(Received March 31, 1966).

ABSTRACT. The luminescence spectra of benzyl acetate in the solid state and in frozen solutions in CCl_4 , chloroform and ethyl alcohol at 93°K excited mainly by 3650 Å group of mercury lines, have been investigated. From reasonable assignments of the band system observed under different conditions it has been concluded that ν_0 band in the luminescence spectrum of the pure solid at 93°K is at 3972 Å and that this may also correspond to the ν_0 band in absorption due to singlet-triplet transition in the molecule of benzyl acetate.

INTRODUCTION

From a detailed investigation of the phosphorescence emitted by solutions of organic compounds in E.P.A. medium at 77°K under excitation from radiations of a high pressure mercury lamp Lewis and Kasha (1944) concluded that the phosphorescence originates from transitions from the excited triplet levels of the molecules to their respective ground states. Similarly, Biswas (1956a, b, c) who studied the luminescence of some pure substituted benzene compounds in the solid state at 93°K excited mainly by the 3650 Å group of mercury lines pointed out that the luminescence has a life time greater than 10^{-3} sec. and might originate from the metastable triplet states of the molecules. However, he could not detect the absorption due to the reverse transition, i.e., from the singlet to triplet levels and only in the case of methyl benzoate somewhat detailed assignments of the observed luminescence bands were possible. It was, therefore, thought that in the cases where $S \rightarrow T$ absorptions bands may not be observed easily, a careful investigation of the phosphorescence spectra and the life times of the emitting levels in a number of related substituted benzene compounds might be helpful in identifying as well as obtaining informations about the triplet levels in such molecules. In this short note a preliminary report of the luminescence bands of pure benzyl acetate in the solid state at different temperatures and of its frozen solutions in various solvents at 93°K has been presented.

EXPERIMENTAL

The sample of benzyl acetate obtained from Société usines Chenuques, France, was first fractionated and the proper fraction was repeatedly distilled under reduced pressure. The solvents used were carbon-tetrachloride, chloroform and ethyl

alcohol. The method of investigation of the luminescence spectra of the pure substance and its solutions in different solvents solidified at about 93°K was the same as that used by Biswas (1956a). A 'Hanovia' type quartz mercury vapour lamp was used as the source of excitation and the Fues glass spectrograph used has dispersions of 12, 20 and 30° Å/mm in the regions of 4047 Å, 4358 Å and 4916 Å respectively. The width of the slit was kept between .15 mm to .50 mm and the times of exposure varied from one hour for the pure substance to ten hours for the dilute solutions. Iron arc spectrum was photographed along with the luminescence bands as comparison in each case.

Microphotometric records of the luminescence spectra and of the comparison iron arc spectrum were taken with a Kipp and Zonen Moll microphotometer. The record from the iron arc spectrum was carefully calibrated and from comparisons of the records of the luminescence bands with that of the iron arc the position of the bands in Å was determined. Measurements of the band-position for a particular sample were made on the records from at least two different plates for the sample. The positions of the bands were determined within 5 Å for the sharp bands and in the case of very weak and broad bands the error in the measurements was about 10 Å.

The Raman and the infrared spectra of pure benzyl acetate in the liquid state were studied and the ultraviolet absorption spectra of the compound in very dilute solutions in carbon tetrachloride and chloroform in the region 4000 Å—2200 Å were also investigated.

RESULTS AND DISCUSSIONS

Some of the microphotometric records of the luminescence bands are reproduced in Figures 1(a) to 1(e) in Plate I. The wavelengths of the bands together with their wavenumbers are given in Tables I and II. The relative intensities and the probable assignments of the bands are also given in the Tables.

It is seen from Figures 1(b) and 1(a) respectively that pure benzyl acetate in the solid state at 173°K shows four bands and when the temperature of the solid is lowered to 93°K the number of the bands increases and also the bands become more intense. With a 10% solution of benzyl acetate in CCl_4 solidified at 93°K, the appearance of the band system is almost similar to that due to the pure solid at the same temperature while a frozen 5% solution in CCl_4 [Fig. 1(c)] shows only the stronger bands. Compared to the spectra of the pure solid at 93°K the luminescence band system of a frozen 10% solution of benzyl acetate in chloroform [Fig. 1(d)] at 93°K are definitely shifted towards the shorter wavelength side while in the case of a 5% solution in alcohol [Fig. 1(e)] under similar condition some of the bands are slightly displaced to the higher wavelengths.

In order to determine the wavelengths of the radiations effective in producing these luminescence bands, the exciting radiations from the quartz mercury vapour

lamp were filtered through filters of aqueous solution of NaNO_2 of different thickness and concentrations (Biswas, 1956d).

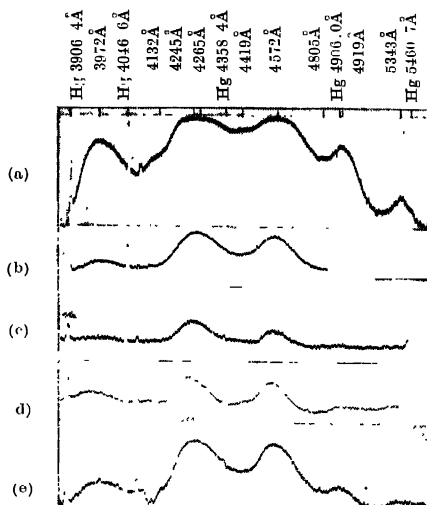


Fig. 1. Luminescence bands of benzyl acetate

- (a) Pure solid at 93°K
- (b) Pure solid at 173°K
- (c) Frozen 5% solution in CCl_4 at 93°K
- (d) Frozen 10% solution in HCCl_3 at 93°K
- (e) Frozen 5% solution in EtOH at 93°K

The gradual weakening of the intensities of the luminescence bands with increasing concentrations of NaNO_2 in the filter solutions indicates that mainly the 3650 Å group of mercury lines and other lines of shorter wavelengths are responsible for producing the luminescence bands.

To find out if the region to the longer wavelength side of 3650 Å would show any absorption band which may be connected with the observed luminescence spectra, the ultraviolet absorption of .1% solutions of benzyl acetate in CCl_4 and in HCCl_3 at room temperature were investigated throughout the wavelength region from 4000 Å to 2200 Å. Strong absorption bands at 2640 Å and 2650 Å respectively due to solutions in CCl_4 and HCCl_3 , probably corresponding to the normal singlet-singlet transition, are observed and the longer wavelength region does not show any appreciable absorption. This inability to detect any absorption band which might be due to $S \rightarrow T$ transition made the assignment of the luminescence bands difficult.

A careful analysis of the band data presented in Tables I and II were, therefore, carried out in order to find out if there were any regularity in the spacings of the bands which might be helpful in making reasonable assignment of the band system.

TABLE I
Luminescence bands of benzyl acetate

Substance	Band maxima in Å	ν in cm^{-1}	Difference from first band in cm^{-1}	Assignment
Pure solid at 173°K	3976 wb	25144		ν_0
	4254 s	23501	1643	ν_0-1604
	4580 s	21828	3316	ν_0-1730
	4955 wb	20176	4968	$\nu_0-1604-1730$ $\nu_0-2 \times 1604-1730$
5% solution in CCl_4 at 93°K	3974 wb	25157		ν_0
	4247 m	23539	1618	ν_0-1604
	4565 m	21899	3258	$\nu_0-2 \times 1604$
10% solution in CCl_4 at 93°K	3971 mb	25176		ν_0
	4133 vw	24187	987	ν_0-1000
	4250 sb	23523	1656	ν_0-1604
				ν_0-1730
	4439 w	22521	2655	$\nu_0-1000-1604$
	4570 sb	21876	3300	$\nu_0-2 \times 1604$
				$\nu_0-1604-1730$
10% solution in HCCl_3 at 93°K	4944 w	20221	4955	$\nu_0-2 \times 1604-1730$
	5372 vwb	18610	6566	$\nu_0-3 \times 1604-1730$
	3962 mb	25223		ν_0
	4237 s	23595	1028	ν_0-1604
5% solution in ethyl alcohol at 93°K	4550 s	21972	3251	$\nu_0-2 \times 1604$
	4912 wb	20353	4870	$\nu_0-3 \times 1604$
	3979 mb	25125		ν_0
	4146 w	24113	1014	ν_0-1000
	4253 s	23506	1619	ν_0-1604
	4560 s	21924	3201	$\nu_0-2 \times 1604$
	4920 m	20320	4805	$\nu_0-3 \times 1604$
	5356 wb	18666	6459	$\nu_0-4 \times 1604$

Intensity: vs—very strong; s—strong; m—medium; w—weak; vw—very weak; b—broad.

The luminescence spectra of the pure solid at 173°K and of the frozen solutions at 93°K show the following characteristics:

i) The shortest wavelength of the luminescence band in each case is at about 3970 Å.

ii) Most of the wavenumber differences between the positions of the band at the shortest wavelength and those of the succeeding bands are found to be such as may be expressed in terms of fundamentals, combinations and overtones mainly of two frequencies—one at about 1600 cm^{-1} and another at about 1700 cm^{-1} .

TABLE II

Luminescence spectrum of benzyl acetate in the solid state at 93°K

Position of Band-maxima in Å	ν in cm^{-1}	Difference from first band in cm^{-1}	Assignment
3972 s	25169		ν_0
4132 m	24195	974	$\nu_0 - 1000$
(4245) (vs)	(23551)	(1618)	$(\nu_0 - 1604)$
4255 vsb	23495	1674	
(4265) (vs)	(23440)	(1729)	$(\nu_0 - 1730)$
4419 m	22623	2546	$\nu_0 - 1000 - 1604$
4572 vsb	21866	3303	$\left. \begin{array}{l} \nu_0 - 2 \times 1604 \\ \nu_0 - 1604 - 1730 \end{array} \right\}$
4805 m	20806	4363	$\nu_0 - 1000 - 1604 - 1730$
4919 s	20324	4845	$\left. \begin{array}{l} \nu_0 - 3 \times 1604 \\ \nu_0 - 2 \times 1604 - 1730 \end{array} \right\}$
5343 m	18711	6458	$\left. \begin{array}{l} \nu_0 - 4 \times 1604 \\ \nu_0 - 3 \times 1604 - 1730 \end{array} \right\}$

Intensity: vs—very strong; s—strong; m—medium; w—weak; vw—very weak, b—broad.

The Raman spectrum of benzyl acetate shows two lines at 1606 and 1750 cm^{-1} and in the infrared spectrum due to the pure liquid two bands at 1602 and 1730 cm^{-1} are observed. These two frequencies obviously correspond to the vibrational modes involving stretching of $\text{C}=\text{C}$ and $\text{C}-\text{O}$ bonds in the molecule of benzyl acetate. On the basis of these two frequencies, the probable assignments of the observed luminescence bands are given in column five of Table I. However, the frequencies involved do not exactly agree with those observed in the infrared and Raman spectra of the compound because of inaccuracies in the measurement of the positions of the broad bands. Due to this reason some of the bands in the spectra of the pure solid at 173°K and of 10% frozen solution in CCl_4 at 93°K have been given two different assignments.

From the above assignments it seems fairly reasonable to identify the band at the shortest wavelength as the ν_0 -band of the luminescence band system. With

3972 Å as the ν_0 -band in the spectrum due to the pure solid at 93°K, the assignment of the other bands has been made (Table II). It is seen from Figure 1(a) that the first very strong band is broad and has its centre at 4255 Å. If it is assumed to consist of two bands at 4250 Å and 4265 Å, they may tentatively be assigned as $\nu_0-1600\text{ cm}^{-1}$ and $\nu_0-1750\text{ cm}^{-1}$ respectively. Similarly, the second very strong band at 4572 Å which is also broad has been assigned both as $\nu_0-2\times 1604\text{ cm}^{-1}$ and $\nu_0-(1604+1730)\text{ cm}^{-1}$. Each of the bands of medium intensity at 4130 Å, 4419 Å and 4805 Å are found to involve a frequency roughly 1000 cm^{-1} corresponding to the breathing carbon vibration of the molecule. This frequency is also found to occur in the luminescence band systems due to the frozen 10% solution of benzyl acetate in CCl_4 and 5% solution in alcohol (Table I). Lastly, the strong band at 4919 Å and the band at 5343 Å of medium intensity have both been given two different assignments.

Though it has not been possible to observe directly the absorption due to $S\rightarrow T'$ transition, the above analysis suggests that in the case of benzyl acetate in the solid state at 93°K the band at 3972 Å may also correspond to the ν_0 -band in absorption. This assignment is justified by the fact that with the lowering of the temperature of the solid from 173°K to 93°K the number and intensity of the bands are considerably increased and no other band at shorter wavelength is observed. The ultraviolet absorption spectra of benzyl acetate in different states and particularly in the solid state at 93°K are being studied to obtain further information on the excited singlet and triplet energy levels of the molecule.

ACKNOWLEDGEMENT

The author is grateful to Professor G. S. Kastha, D.Sc., for his active interest and continued guidance throughout the progress of the work.

REFERENCES

- Biswas, D. C., 1956 a, b, c, d, *Indian J. Phys.*, **30**, 143, 407, 565, 255.
Lewis, G. N. and Kasha, M., 1944, *J. Am. Chem. Soc.*, **67**, 991.